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Donor-extended tripodal pyrroles: encapsulation, metallation, and H-bonded tautomers **

John S. Hart,¹ Fraser J. White¹ and Jason B. Love^{1,*}

^[1]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

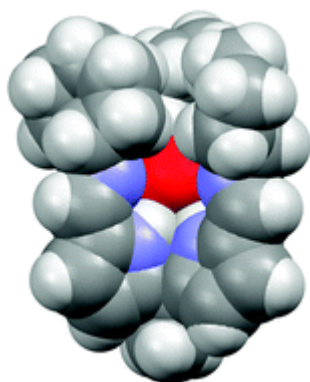
^[*]Corresponding author; e-mail: jason.love@ed.ac.uk; fax: +44 (0)131 6504743

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^[†]Electronic Supplementary Information (ESI) available: full experimental data and crystal data for CCDC 816434 to 816437. See <http://dx.doi.org/10.1039/C1CC11378J>

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molecular recognition; crystal-structure; water; oxygenation; selectivity; reactivity; receptors; chemistry; oxidation; cavities

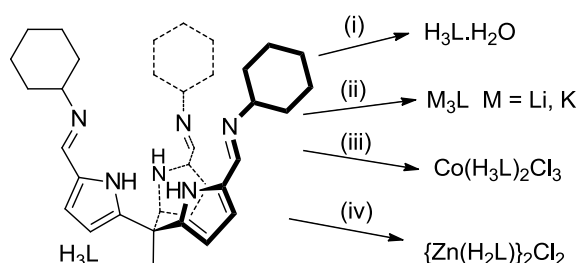
Abstract

A tripodal iminopyrrole provides an environment suited to the encapsulation of water through hydrogen-bonding, and the formation of metal complexes by deprotonation and imine-pyrrole tautomerisation.

Main text

The development of ligands that can define both the primary and significantly, the secondary coordination spheres of metals through substrate encapsulation, π -interactions or hydrogen bonding is becoming increasingly important to the design of new catalysts. In part this reflects a deeper appreciation of metalloenzyme chemistry in which it has long been recognised that secondary structure plays a crucial role in enzyme-mediated reactions,¹ and which has led to the burgeoning field of supramolecular catalysis.² The addition of hydrogen bonding donor and acceptor appendages to ligands has been shown to change dramatically metal-mediated reaction pathways,³ and furthermore, encapsulation by the host provides an unusual guest microenvironment that effects the stability of reagents and the efficacy and selectivity of chemical reactions.⁴

We have shown previously that the addition of M^{II} halides ($M = \text{Fe}, \text{Co}, \text{Zn}$) to imine-functionalised dipyrromethanes resulted in pyrrole-nitrogen metallation with associated imine-pyrrole to amine-azafulvene tautomerisation; this latter aspect formed a new ligand environment that engaged in hydrogen-bonding with ancillary halide and azide ligands.⁵ Tautomerisation to form a C_3 -hydrogen-bonding cavity on metallation has also been seen using tripodal aminooxazoline ligands.⁶ We report here on the use of the tripodal iminopyrrole H_3L as a platform for generating an environment for encapsulation, metallation, and hydrogen-bonding interactions. This compound was described previously by Beer and co-workers as a construct in the synthesis of dithiocarbamate cages and pyrrole cryptands,⁷ and, furthermore, simple tripodal pyrroles have been shown to exhibit interesting chemistry on metallation.⁸



Scheme 1. Reactions of the donor-extended tripodal pyrrole H_3L . Reagents and conditions: (i) recrystallise $\text{CH}_3\text{CN}/\text{H}_2\text{O}$, 92%; (ii) 3 $\text{LiN}(\text{SiMe}_3)_2$, THF, 88 % or KH , THF, 90%; (iii) CoCl_2 , EtOH, 88 %; (iv) ZnCl_2 , MeOH, NEt_3 , 26 %.

The pro-ligand H_3L was synthesised according to the literature⁷ and was isolated as a crystalline material from hot CH_3CN as the monohydrate $H_3L \cdot H_2O$ (Scheme 1).[‡] The X-ray crystal structure of $H_3L \cdot H_2O$ was determined (Fig. 1) and highlights the propensity of the pyrrole and imine groups to act as hydrogen-bond donors and acceptors respectively, resulting in a C_3 -symmetric host within which the single guest molecule of water is bound. The structure was best solved with the addition of a disorder component as a result of three-fold rotation at the apical carbon; this resulted in two orientations of each pyrrole-imine arm and overall a relatively poor refinement. The imine $C=N$ bond distance ($N2-C7$ 1.24(2) Å) is indicative of double bonding, and combined with the other pyrrole geometric data suggests that the imine-pyrrole tautomer is retained on water binding. This is reinforced by the 1H NMR spectrum of $H_3L \cdot H_2O$ in $CDCl_3$ which displays standard imine and pyrrole resonances and not those associated with the tautomeric form (see later).

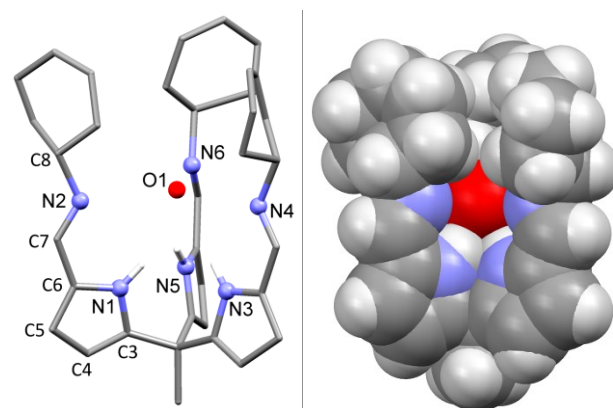


Figure 1. Ball and stick (left) and space-filled representations (right) of the X-ray crystal structure of $H_3L \cdot H_2O$. For clarity, disorder components and all hydrogen atoms except on N1, N3, and N5 are omitted. Selected bond lengths (Å): N1-C3 1.39(2); C3-C4 1.31(5); C4-C5 1.40(7); C5-C6 1.34(4); C6-N1 1.33(4); C6-C7 1.48(3); C7-N2 1.24(2); C8-N2 1.51(3); N1 \cdots O1 3.12(2); N2 \cdots O1 2.87(2).

The directionality of hydrogen bonding allows water molecules to play important structural and functional roles in enzymatic and biomimetic chemistry, and is a motif that is increasingly being used as a design element in molecular engineering.⁹ In our case, it is clear that the presence of water during crystallisation of H_3L has resulted in the orientation of the three arms of the pro-ligand around the water molecule, so forming an unusual, sterically-protected, hydrophilic pocket.

Significantly, host molecules such as calixarenes and open-cage fullerenes normally project a hydrophobic surface to their guest molecules,¹⁰ and the construction of host molecules that incorporate internal polar or hydrogen-bonding sites, sometimes known as inverted molecular capsules, is not straightforward.¹¹

Deprotonation reactions between H_3L and the strong bases KH and $\text{LiN}(\text{SiMe}_3)_2$ were carried out and led cleanly to the alkali metal complexes M_3L ($\text{M} = \text{K}, \text{Li}$) (Scheme 1).[‡] The ^1H NMR spectra of both K_3L and Li_3L in $\text{C}_6\text{D}_6/\text{THF}$ mixtures support C_3 -symmetrical products in solution with resonances at 8.13, 6.53 and 6.15 ppm for K_3L consistent with one imine and two pyrrole environments. However, the X-ray crystal structure of Li_3L after crystallisation from THF/hexane shows that the new product $[\text{Li}_3(\text{THF})_3(\text{LiOH})_3(\text{L})]_2$ had formed, presumably through trace hydrolysis by adventitious amounts of water (Fig. 2). In this structure, the Li cations adopt pseudo-tetrahedral geometries and are found in two coordination environments with Li1, Li2 and Li3 each bound by two pyrrolide nitrogens, a THF oxygen and a OH oxygen. The remaining Li cations Li4, Li5, and Li6 form part of a $\{\text{LiOH}\}_6$ cluster derived from two stacked six-membered Li_3O_3 rings of chair conformations. Overall, the core structure is best described as a hexameric $\{\text{LiOH}\}_6$ cluster capped on each face by three Li cations. Additional Li-bonding to the imine nitrogens is seen, and results in complete encapsulation of the Li/LiOH core by the organic framework in which the cyclohexyl rings interdigitate. Lithium alkoxides are well known to form similar hexameric structures in which two $\text{Li}_3(\text{OR})_3$ rings stack in a chair conformation, and Li-capped structures have also been reported.¹² However, $[\text{Li}_3(\text{THF})_3(\text{LiOH})_3(\text{L})]_2$ represents the first $\{\text{LiOH}\}_6$ cluster that is triply-capped by Li cations on both hexagonal faces and is presumably stabilised by the encapsulating organic framework.

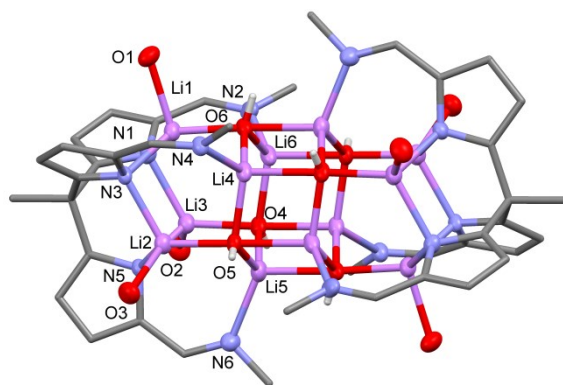


Figure 2. X-ray crystal structure of $[\text{Li}_3(\text{THF})_3\text{L}(\text{LiOH})_3]_2$. For clarity, cyclohexyl carbon atoms, disorder components, and all hydrogen atoms except those on O4, O5, and O6 are omitted (50% probability displacement ellipsoids where drawn). Selected bond lengths (Å): Li1-N1 2.069(6); Li1-N3: 2.076(6); Li1-O1 2.058(6) Li1-O6 1.920(5); Li4-N4 2.078(6); Li4-O4' 2.063(5); Li4-O5 1.928(6); Li4-O6 1.915(6).

While salt elimination reactions between Li_3L and transition-metal salts such as ZrCl_4 have, as yet, proved inconclusive, the addition of CoCl_2 to H_3L under aerobic conditions resulted in the formation of the new Co^{III} complex $[\text{Co}(\text{H}_3\text{L})_2][\text{Cl}]_3$ (Scheme 1)[‡] in which the two ligands bind to the single metal in a

manner similar to tris(pyrazolyl)borates. The oxidation of Co^{II} to Co^{III} is supported by the diamagnetic ^1H NMR spectrum (Fig S1, ESI), which also suggests that ligand tautomerisation has occurred on metallation with the appearance of new doublet resonances at 7.45 and 6.89 ppm for the amine-azafulvene conformer. The X-ray crystal structure of $[\text{Co}(\text{H}_3\text{L})_2][\text{Cl}]_3$ (Fig. 3) confirms that tautomerisation has occurred on metallation with, in particular, an elongation of N2-C7 (1.290(7) Å) compared to N2-C7 (1.24(2) Å) in $\text{H}_3\text{L} \cdot \text{H}_2\text{O}$. The cobalt cation adopts octahedral geometry with each H_3L ligand facial. The ligand branches are in an *anti*- conformation and interlock through hydrogen bonding to a total of six chloride anions, three of which arise from extension of the solid state structure.

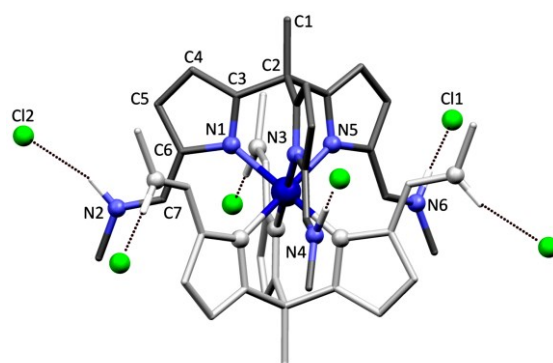


Figure 3. Ball and stick representations of the X-ray crystal structure of $[\text{Co}(\text{H}_3\text{L})_2][\text{Cl}]_3$. For clarity, all hydrogen atoms, cyclohexyl carbons and disorder components are omitted. Selected bond lengths (Å) and angles ($^\circ$): Co1-N1 1.953(3); Co1-N3 1.956(3); Co1-N5 1.945(3); N2 \cdots Cl2 3.167(6); N4 \cdots Cl2 3.149(5); N6 \cdots Cl1 3.167(6); N1-Co1-N3 88.44(14).

A similar reaction between ZnCl_2 and H_3L , in this case in the presence of NEt_3 results in the formation of the binuclear zinc complex $[\text{Zn}_2(\text{H}_2\text{L})_2][\text{Cl}]_2$. ‡ In the X-ray crystal structure (Fig. 4), the zinc cations are tetrahedral and both coordinated to pyrrolide and imine nitrogens of one ligand and to two pyrrole nitrogens of the other, so forming a dimer in which two of the branches of L are tautomerised while the remaining branch is deprotonated; this results in a $\text{Zn} \cdots \text{Zn}$ separation of 4.245 Å. The partial tautomerisation of L is supported by the differences in N2-C7 (1.327(6) Å) and N4-C18 (1.312(6) Å) bond distances compared to N6-C29 (1.291(6) Å) and also by the hydrogen-bonding interactions between the protons located on N2 and N4 and the chloride anions. Furthermore, the ^1H NMR spectrum of $[\text{Zn}_2(\text{H}_2\text{L})_2][\text{Cl}]_2$ (Fig. S2, ESI) shows that the solid state structure is retained in solution, with two distinct sets of resonances in a 2:1 ratio due to two tautomerised pyrrole-imine branches (NH: 10.2 ppm, $^3J_{\text{HH}} = 15.1$ Hz; CH 6.50 ppm) and a single deprotonated branch (pyrrole CH 6.67 and 6.80 ppm, imine CH 8.10 ppm). The ESMS spectrum of $[\text{Zn}_2(\text{H}_2\text{L})_2][\text{Cl}]_2$ displays a peak at m/z 1234 in positive ion mode

consistent with the molecular ion of the binuclear structure, and fragmentation to the monomeric species $\text{Zn}(\text{H}_2\text{L})$ at m/z 618, suggesting that the binuclear motif is potentially labile. Linked pyrroles have been seen previously to form binuclear zinc complexes, in particular forming helicates and mesocates,¹³ although in contrast to $[\text{Zn}_2(\text{H}_2\text{L})_2][\text{Cl}]_2$ which has undergone partial tautomerisation, these complexes are unable to partake in secondary interactions.

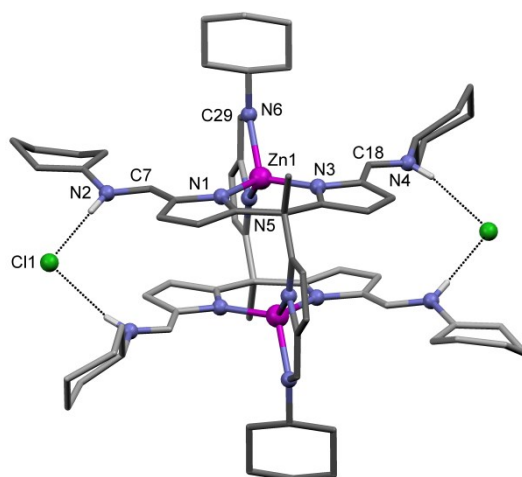


Figure 4. Ball and stick representation of the crystal structure of $[\text{Zn}_2(\text{H}_2\text{L})_2][\text{Cl}]_2$. For clarity, disorder components and all hydrogen atoms except those on N2 and N4 are omitted. Selected bond lengths (Å) and angles (°): Zn1-N1 1.977(4); Zn1-N3 1.963(4); Zn1-N5 2.006(4); Zn1-N6 2.063(4); Zn1 \cdots Zn2 4.2488(8); N2 \cdots Cl1 3.173(4); N4 \cdots Cl1 3.198(5) N1-Zn1-N3 96.0(2); N1-Zn1-N5 122.5(2); N1-Zn1-N6 116.1(2); N5-Zn1-N6 83.8(2).

We have shown that the addition of imine substituents to a tripodal pyrrole results in a versatile platform for both metallation and supramolecular interactions. In particular, the tautomerisation on metallation exhibited here to form hydrogen-bonding appendages is under-utilised in general and represents a potentially wide-ranging method for addressing the secondary coordination sphere in metal complexes.

Notes and references

‡Syntheses and crystal data: H_3L Colourless solid in 92 % yield (0.89 g). Analysis. Found: C, 75.99; H, 8.89; N, 15.16% $\text{C}_{35}\text{H}_{48}\text{N}_6$ requires C, 76.05, H, 8.75, N, 15.20%. Single crystals were grown from cooling of a saturated MeCN solution: $\text{C}_{35}\text{H}_{50}\text{N}_6\text{O}$, M 570.8, trigonal $R3$, $a=b=14.6784(2)$, $c=12.8656(2)$ Å, $\alpha=\beta=90$, $\gamma=120^\circ$, V 2400.59(6) Å³, 150(2) K, $Z=3$, 940 independent reflections, $R(\text{int})$ 0.026, $R[F^2 > 2\sigma(F^2)]$ 0.065, CCDC 816434. $[\text{Li}_3(\text{THF})_3(\text{LiOH})_3(\text{L})]_2$ Colourless crystals grown from slow diffusion of hexane into a saturated THF solution at -20°C : $\text{C}_{100}\text{H}_{156}\text{Li}_{12}\text{N}_{12}\text{O}_{13.50}$, M 1825.65, monoclinic $P2_1/c$, $a=14.2257(5)$, $b=20.6980(6)$, $c=20.3016(6)$ Å, $\beta=109.511(4)^\circ$, V 5634.4(3) Å³, 150(2) K, $Z=2$, 13199 independent reflections, $R(\text{int})$ 0.033, $R[F^2 > 2\sigma(F^2)]$ 0.076, CCDC 816435. $[\text{Co}(\text{H}_3\text{L})_2][\text{Cl}]_3$ Green solid in 45% yield (0.026 g). Single crystals were grown by Et_2O diffusion into a saturated MeOH solution: $\text{C}_{70}\text{H}_{88}\text{CoN}_{12}\text{Cl}_3$, M 1262.80, monoclinic $C2/c$, $a=31.439(5)$, $b=14.0249(7)$, $c=22.558(4)$ Å, $\beta=130.79(3)^\circ$, V 7531(4) Å³, 150(2) K, $Z=4$, 6406 independent reflections, $R(\text{int})$ 0.051, $R[F^2 > 2\sigma(F^2)]$ 0.075, CCDC 816436. $[\text{Zn}_2(\text{H}_2\text{L})_2][\text{Cl}]_2$ Colourless solid in 26% yield (0.32 g). Analysis. Found: C, 64.49, H, 7.24, N, 12.72% $\text{C}_{70}\text{H}_{94}\text{Cl}_2\text{N}_{12}\text{Zn}_2$ requires C, 64.41, H, 7.26, N, 12.88% Single crystals were grown from Et_2O diffusion into a saturated solution of THF at -25°C : $\text{C}_{78}\text{H}_{110}\text{N}_{12}\text{O}_2\text{Zn}_2\text{Cl}_2$, M 1449.42, monoclinic $P2_1/c$, $a=13.6569(4)$, $b=25.0290(8)$, $c=10.9583(4)$ Å, $\beta=96.887(3)^\circ$, V 3718.7(2) Å³, 150(2) K, $Z=4$, 7361 independent reflections, $R(\text{int})$ 0.101, $R[F^2 > 2\sigma(F^2)]$ 0.097, CCDC 816437.

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